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Title: Solid Phase Extraction of Nitroaromatic and Nitroamine Explosive Compounds and Picric Acid from Water Samples [SW-846 3535A]

Facility Distribution No. _____ **Distributed To:_____**

1.0 Scope and Application

1.1 This standard operating procedure (SOP) describes the extraction of nitroaromatic and nitroamine explosive residues by solid phase extraction (SPE). This procedure is based on SW-846 method 3535A.

1.2 This procedure does not describe the analysis of the extracts. For those details, see the following SOPs:

1.2.1 DV-LC-0002 "*Analysis of Nitroaromatic and Nitroamine Explosive Compounds by HPLC"*

1.2.2 DV-LC-0010 "*Analysis of Nitroaromatic and Nitroamine Explosives Compounds by APCI/LC/MS"*

2.0 Summary of Method

2.1 Aqueous samples undergo solid phase extraction (SPE). For samples that are to be analyzed by method 8330A or 8330B, 25 g of NaCl is added to a 500 mL sample aliquot and extracted. For samples that are to be analyzed by method 8321A or 8321B LC/MS, a 1000 mL aliquot is extracted. The analytes are absorbed onto the sorbent material in the SPE cartridge, and then eluted with 2.5 mL of 0.1% acetic acid in acetonitrile. The concentrated extract is diluted 1:1 with an aqueous solution of calcium chloride prior to analysis by method 8330A or 8330B or with water prior to analysis by method 8321A or 8321B.

3.0 Definitions

3.1 Refer to the Glossary of the TestAmerica Denver Quality Assurance Manual (QAM) and policy DV-QA-003P, Quality Control Program, for definitions of general analytical and QA/QC terms.

3.2 Explosives: As used in this SOP, the term "explosives" refers specifically to the analytes listed in the Tables. These include compounds that can be readily detonated with heat, shock, or ignition, such as nitroglycerin, RDX, and TNT. It also includes production by-products and degradation products of true explosives.

3.3 SPE: Solid Phase Extraction

3.4 LIMS: Laboratory Information Management System

4.0 Interferences

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by running method blanks.

4.2 Contamination by carryover can occur when a low-concentration sample is analyzed immediately following a high-concentration sample.

4.3 The extraction of high-level samples can cause contamination in the extractions lab, especially on the solid-phase manifold. If water samples appear to have a red tint or if the extracts appear to be multi-phasic, the project manager and client should be contacted and care should be taken to minimize cross-contamination.

4.4 It has been determined that tetryl can adhere to the cartridge in such a manner that pure acetonitrile will not elute the compound off of the cartridge packing. It is surmised that tetryl may become ionized in the extraction procedure and adhere more tightly to the cartridge packing than the other explosives. Therefore the elution is performed with 0.1% acetic acid in acetonitrile. The lab has demonstrated increased recoveries for tetryl when this slightly acidic elution solvent is used.

4.5 Samples with suspended solids or sediment can cause the extraction cartridge to clog. It may be necessary to filter the samples before extraction to prevent this. If a sample is filtered prior to extraction, an NCM should be written.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2 Specific Safety Concerns or Requirements

Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated will be removed and discarded; non-disposable gloves must be cleaned immediately.

5.3 Primary Materials Used

5.3.1 The following is a list of materials used in this method, which have a serious or significant hazard rating.

NOTE: This list does not contain all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.

5.3.2 A complete list of materials used in the method can be found in the reagent and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

MATERIAL (1)	HAZARDS	EXPOSURE LIMIT (2)	SIGNS AND SYMPTOMS OF EXPOSURE
ACETONITRILE	FLAMMABLE	40 PPM – TWA	Early symptoms may include nose and throat irritation,

MATERIAL (1)	HAZARDS	EXPOSURE LIMIT (2)	SIGNS AND SYMPTOMS OF EXPOSURE
	POISON		flushing of the face, and chest tightness. Prolonged exposure to high levels of vapors may cause formation of cyanide anions in the body.
METHANOL	FLAMMABLE POISON IRRITANT	200 PPM - TWA	A slight irritant to the mucous membranes. Toxic effects are exerted upon the nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness, and dizziness. Methyl alcohol is a defatting agent and may cause the skin to be become dry and cracked. Skin absorption can occur, symptoms may parallel inhalation exposure. Irritant to the eyes.
PHOSPHORIC ACID	CORROSIVE	1 PPM - TWA	Ingestion can cause severe burns to the throat, mouth, and stomach, abdominal pain and nausea. Severe exposures by ingestion can lead to shock, circulatory collapse, and death. Inhalation is not an expected hazard unless misted. Corrosive, contact with skin or eyes can cause redness, pain, severe burns, blurred vision, and permanent eye damage.
ACETIC ACID, GLACIAL	CORROSIVE POISON FLAMMABLE	10 PPM – TWA	Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur. Can cause serious damage to the skin, including redness, pain, and burns. Contact with eyes may cause severe damage followed by loss of sight.
METHYLENE CHLORIDE	CARCINOGEN IRRITANT	25 PPM (TWA) 125 PPM (STEL)	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting, and headache. Causes irritation, redness, and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.

(1) ALWAYS ADD ACID TO WATER TO PREVENT VIOLENT REACTIONS.

(2) EXPOSURE LIMIT REFERS TO THE OSHA REGULATORY EXPOSURE LIMIT.

6.0 Equipment and Supplies

6.1 Equipment

All equipment IDs for any support equipment (pipettes, thermometers, etc.) must be recorded in the batch record.

6.1.1 Vacuum manifold for SPE cartridges. Capable of maintaining approximately 66 cm (26”) of Hg. After each use, the valves and tube caps are removed from the manifold, set to the open position and placed in a jar with acetonitrile. The jar is placed into a sonication bath for a minimum of 30 minutes. The jar used to sonicate the valves should be replaced at least weekly to avoid contamination.

6.1.2 Nitrogen evaporation apparatus (N-EVAP) for the concentration of some water extracts.

6.1.3 Balance capable of measuring ± 0.1 g. Calibration checked per SOP DV-QA-0014. Used to measure the initial sample mass and volume.

6.1.4 Pipettor with disposable 1.0 mL tips. Calibration checked per SOP DV-QA-0008. Used to add surrogate and spike standards to samples.

6.1.5 Pipettor with disposable 0.1 mL tips. Calibration checked per SOP DV-QA-0008. Used to add surrogate and spike solution to samples.

6.1.6 Pipettor capable of dispensing 5 to 50 mL. Calibration checked per SOP DV-QA-0008. Used to calibrate vials to hold 5 mL for the final volume determination for water extracts.

6.2 Supplies

6.2.1 pH paper, wide range.

6.2.2 Volumetric Flasks and Graduated Cylinders, glass, Class A, various sizes

6.2.3 Amber Glass Vials, 8.0 mL, with Teflon-lined screw caps. For the storage of final extracts. Vials used to store the final extracts are calibrated to hold a volume of 5 mL by using a calibrated pipette to deliver 5 mL of acetonitrile into the vial, and marking the meniscus with a fine-tipped permanent marker. This volume is accurate to ± 2%.

6.2.4 Disposable pipettes, used for non-quantitative transfers only.

6.2.5 SPE Cartridges for method 8330A and 8330B (PoraPak RDX 6 cc tubes, Waters part no. WAT047220)

6.2.6 SPE Cartridges for method 8321A and 8321B (Strata SDB-L 500 mg packed into 6 mL tubes, Phenomenex part no. 8B-S014-HCH)

6.2.7 SPE tubing, non-PTFE in composition, with weights attached to one end. Tubes are cleaned before and after each use with acetonitrile followed by reagent water.

6.2.8 Miscellaneous laboratory apparatus (beakers, filter flasks, Büchner funnels, volumetric flasks, pipettes etc.). These should be disposable where possible, or marked and segregated for high-level versus low-level use.

6.2.9 Glass fiber filter paper, Ahlstrom, catalog number 1510-0900 or equivalent.

6.3 Computer Software and Hardware

Please refer to the master list of documents, software and hardware located on R:\QA\Read\Master List of Documents\Master List of Documents, Software and

Hardware.xls or current revision for the current software and hardware to be used for data processing.

7.0 Reagents and Standards

7.1 Reagent Water – TestAmerica Denver has three ELGA Analytical water purification systems equipped with UV lamps. The water coming from the ELGA system should be 18-18.2 Mohm-cm. The performance of the water polishing system is checked daily and recorded per SOP DV-QA-0026.

7.2 Acetonitrile, CH_3CN - HPLC grade (ACN) – Each lot of solvent is tested following CA-Q-S-001-DV-1. QA personnel post the list of approved lots at solvent storage areas.

7.3 Phosphoric acid, 85% H_3PO_4 (Phosphor Acid)– Purchased ready to use. Used to make up the $CaCl_2$ Solution in Section 7.4**.**

7.4 Calcium Chloride Solution, 5 g/L (CaCl2_Sol) - Used to bring the 8330A and 8330B extracts up to volume.

Place 5 ± 0.05 g of reagent grade $CaCl_2$ into a one-liter volumetric flask containing approximately 500 mL of reagent water. Swirl the solution until the $CaCl_2$ is dissolved. Add approximately 1 mL of 85% H_3PO_4 to acidify the solution and make up to volume with reagent water.

7.5 Approximately 0.1% Acetic Acid in Acetonitrile (0.1%AAinACN) – Open a new 4-liter bottle of acetonitrile and add 4 mL of acetic acid. Cap and mix. This reagent is given a 1 year expiration date.

7.6 Baked Sodium Chloride – Added to 8330A or 8330B samples to facilitate the extraction of picric acid.

Bake in 400 °C oven for at least 4 hours.

7.7 Methylene Chloride – Used to pre-condition the SPE cartridges.

7.8 Standards

7.8.1 Please reference SOP DV-OP-0020 and WI-DV-009 for information regarding the surrogate and spike standards used in this procedure.

7.8.2 The LCS standards should remain in the freezer for storage. The standard is to be brought to room temperature before use.

8.0 Sample Collection, Preservation, Shipment and Storage

Method	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
8321A or 8321B	Amber glass; Teflon caps	1 Liter	Cool. ≤ 6°C, not frozen	7 Days	SW-846 8330B
8330A or 8330b	Amber glass; Teflon caps	500 mL	Cool. ≤ 6°C, not frozen	7 Days	SW-846 8330B

[1] Exclusive of Analysis.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS Method Comments to determine specific QC requirements that apply. For SOPs that address only preparation, QC acceptance limits on the analytical results are not included. Refer to the appropriate SOP that describes the determinative method.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, *Quality Control Program*.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), etc., are described in TestAmerica Denver policy DV-QA-024P, *QA/QC Requirements for Federal Programs*. This procedure meets all criteria for DoD QSM 5.0 unless otherwise stated. Any deviation or exceptions from QSM 5.0 requirements must have prior approval in the project requirements.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in the LIMS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Initial Performance Studies

Before analyzing samples, the laboratory must establish a method detection limit (MDL). In addition, an initial demonstration of capability (IDOC) must be performed by each analyst on the instrument he/she will be using. On-going proficiency must be demonstrated by each

analyst on an annual basis. See Section 12.0 for more details on detection limit studies, initial demonstrations of capability, and analyst training and qualification.

9.3 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. The method blank must be run on each instrument that is used to analyze samples from the same preparation batch. See Policy DV-QA-003P for further details.

9.4 Method Blank (MB)

At least one method blank must be processed with each preparation batch. The method blank consists of reagent water, which is free of any of the analyte(s) of interest. The method blank is processed and analyzed just as if it were a field sample.

9.5 Laboratory Control Sample (LCS)

9.5.1 One LCS must be processed with each preparation batch. (See section 9.6.2) The LCS consists of reagent water to which the analyte(s) of interest are added at known concentration. The LCS is carried through the entire analytical procedure just as if it were a sample.

NOTE: If insufficient sample volume is available for MS/MSD, an NCM must be written and a LCSD must be prepared.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.6.1 One MS/MSD pair must be processed with each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. It is prepared in a manner similar to the LCS, but uses a real sample matrix in place of the blank matrix. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked exactly as the MS) that is prepared and analyzed along with the sample and matrix spike. Some programs allow spikes to be reported for project-related samples only. Samples identified as field blanks cannot be used for the MS/MSD analysis.

9.6.2 If insufficient sample volume is available for MS/MSD, an NCM must be written and a LCSD must be prepared.

9.7 Surrogate Spikes

Every calibration standard, field sample, and QC sample (i.e. method blank, LCS, LCSD, MS, and MSD) is spiked with surrogate compounds.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.3 Clean the SPE manifold and tubing - Pull acetonitrile, followed by water from the ELGA system, through each tube and each port on the vacuum manifold.

NOTE: For method 8321A and 8321B be sure to use the Strata SDB-L cartridges. For method 8330A and 8330B be sure to use the PoraPak RDX cartridges.

10.4 Precondition the SPE cartridge

10.4.1 **For method 8330:** Fill each cartridge two times with methylene chloride (12 mL total) and draw it through the column by gravity. Only when the solvent stops dripping, then use a vacuum to pull the rest of the solvent through. Empty the in-process tank into waste stream B. Then fill each cartridge two times with acetonitrile (12 mL total) and draw it through the column using a vacuum manifold. Empty the in-process tank into waste stream C

10.4.2 **For method 8321:** Fill each cartridge two times with acetonitrile (12 mL total) and draw it through the column using a vacuum manifold. Empty the in-process tank into waste stream C.

10.5 Condition the SPE cartridge - Fill the cartridge four times with reagent water and draw the water through the cartridge. Fill the cartridge a fifth time and close the valve to prevent the water from dripping through. Cap each cartridge using clean and dry caps.

10.6 Prepare MBs and LCSs – For every MB and LCS sample by method 8330A and 8330B, place 500 mL of reagent water in a disposable 500 mL Boston round bottom bottle. For every MB and LCS sample by method 8321A and 8321B, place 1000 mL of reagent water in a disposable 1000 mL Boston round bottle.

NOTE: Rotate glassware; do **not** use specific glassware or positions for the MB and LCS/LCSD.

10.7 Inspect the water sample for the presence of sediment. The sample must be free of particulate matter before it is introduced into the SPE extraction cartridge. Particulate matter will obstruct the media and cause the analysis to fail. If the samples are particulate

free, proceed to Section 10.9. If the samples have sediment or suspended solids, proceed to Section 10.8.

10.8 Filter Samples with Solids. If the sample contains suspended solids or settled solids that will likely clog the solid phase cartridge, then the sample can be vacuum filtered though glass fiber filter paper to separate the solids from the water. Rinse a filter flask and a Büchner funnel lined with filter paper once with acetonitrile and twice with water. Under vacuum, filter the sample. Do not rinse the original sample container as this will incorrectly raise the initial volume of the sample. If there is no sediment remaining in the original sample container, return the sample to the original sample container. Whenever possible, the sample should be extracted directly from the original sample container. This will allow the sample container to be rinsed. If the original sample container contains sediment, the sample can be extracted in the filter flask. Write an NCM stating that the sample had to be filtered to remove suspended solids.

10.9 Aliquot 8330 Samples received in 1 L ambers - Whenever possible, the sample should be extracted directly from the original sample container. This will allow the sample container to be rinsed at the end of the procedure. If the original sample container is a 1000 mL container and the requested method is 8330A or 8330B, then a 500 mL aliquot should be transferred to a new disposable 500 mL amber bottle. Write a NCM to document that the rinse of the original sample container could not be performed. Follow the procedures in Section 10.10 to aliquot either gravimetrically or volumetrically.

10.10 Aliquot Samples - It is the laboratory's standard procedure to aliquot samples gravimetrically. Check the Method Comments to see if volumetric aliquotting is required.

10.10.1 Aliquot Gravimetrically - Weigh the full sample bottle (either the original container or the filter flask) to the nearest gram using a top loading balance, and record the weight on the benchsheet. After the extraction, weigh the empty sample bottle, and record the weight. Subtract the empty bottle weight from the full bottle weight and record the difference as the sample volume in mL. If the initial volume is less than the nominal volume by 20% or more, prepare an NCM. If there is any indication that the density of the sample is not 1 g/mL, measure the density of the sample using a calibrated pipette and refer to Section 11.2. Proceed to Section 10.11.

10.10.2 Aliquot Volumetrically - For each sample, rinse a Class A graduated cylinder (500 mL for 8330, 1000 mL for 8321) once with acetonitrile and twice with reagent water. Carefully pour the sample from the original container into the graduated cylinder, making sure that if any sediment is present, it is not transferred to the graduated cylinder. Record the volume to the nearest 10 mL. If the initial volume is less than the nominal volume by 20% or more, prepare an NCM. Transfer the sample back to the original sample container. Rinse the graduated cylinders with reagent water and add the rinse to the sample. If sediment was present in the original sample container the sample can be transferred from the graduated cylinder into a new amber glass bottle. Write a NCM to document that the rinse of the original sample container could not be performed. Place the original sample bottle beside the new sample bottle so a second analyst can check that the correct sample was aliquotted. Proceed to Section 10.11.

10.11 Add Surrogate Standards to Sample Containers - Add surrogate standard to each field sample and QC sample using a calibrated pipette. Reference WI-DV-009 to determine the correct surrogate standard and the correct volume to be used. The surrogate standard should be added to the sample in the original sample container unless the sample had significant sediment, was received in the improper container, or aliquoted volumetrically. Record the ID of the standard and the pipette used on the bench sheet.

10.12 Add Spike Standards to Sample Containers - Add spike standard to each LCS, MS, and MSD sample using a calibrated pipette. Reference WI-DV-009 to determine the correct spike standard and the correct volume of standard to be used. The spike standard should be added to the MS and MSD samples in the original sample containers unless the sample had significant sediment or was received in the improper container. Record the ID of the standard and the pipette used on the bench sheet.

NOTE: The addition of spikes and surrogates to samples must be done only immediately after a second analyst has reviewed the batch. Reference work instruction WI-DV-009. Also at this time the witness checks the sample labels to ensure samples are correctly identified.

10.13 Salt the Samples for method 8330A and 8330B -- For methods 8330A and 8330B add 25 g of baked Sodium Chloride to every field sample and QC samples. This is done to facilitate the extraction of picric acid.

10.14 Cap the samples and mix to ensure the salt and the surrogate and spike standards are mixed into the sample completely.

10.15 Connect the Tubing - Using the tubing that has been rinsed with acetonitrile and water, connect the cartridge to the sample container. If the extraction is being performed directly from the sample container care should be taken if there are solids that have settled to the bottom of the bottle. Clip the tubing so that the end is not resting on the bottom, but suspended above the solids.

10.16 Load the Sample onto the Cartridge

10.16.1 Begin drawing the sample through the cartridge at a rate of approximately 10 mL/minute. The solution should come out of the cartridge as individual drops. If the sample comes out of the cartridge in a stream instead of drops, the elution rate is too fast. 10 mL/minute is approximately 45 drops every 15 seconds.

10.16.2 Do not let the extraction tube go completely dry.

10.16.3 A cartridge is considered clogged if a flow rate of 4 mL/min cannot be achieved. This is approximately 1 drop every second. If the cartridge clogs during sample loading, a second cartridge can be used for the sample and then extracts are combined. Alternatively, measure the amount of sample successfully extracted, and use that volume for the extraction constant. If this approach is used, then the surrogate and spike volumes must be corrected for the new initial volume. See Section 11 on how to calculate the actual surrogate and spike volumes.

10.16.4 As the sample level drops, rinse the walls of the sample container with reagent water. After all of the sample and the water used to rinse the container has gone through the line, close the valve and remove the line and the cap from the cartridge. It is important not to let the cartridge go dry, but to leave water in the cartridge.

10.17 Wash the Cartridge – After all samples have passed through the cartridge and valves have been closed and all lines and caps have been removed from the cartridges, rinse each cartridge two times with the reagent water by filling the cartridges with the water and opening the valves and drawing it through with the vacuum. Do not allow the cartridge to go dry, but do not leave any solution remaining above the glass frit that sits on top of the column packing.

10.18 Elute the Cartridge

10.18.1 Turn off the vacuum and remove the manifold lid. Wipe the needles dry with a laboratory tissue being careful not to spread contamination from needle to needle. The tissue used can be wetted with acetonitrile. Place the lid on a clean lab tissue. Place the vial holder inside the manifold and place 8 mL amber vials that have been calibrated to 5 mL inside the manifold on top of the vial holder. Replace the manifold lid and be sure that each valve needle is positioned inside a vial.

10.18.2 Using a serological pipette or a bottle-top re-pipettor, add 2.5 mL of 0.1% acetic acid in acetonitrile to each cartridge. Turn on the vacuum pump while the valves on the manifold are still closed, then quickly open and close each valve to create a vacuum in the cartridges. Turn off the vacuum pump and break the vacuum in the manifold. Open the valves to allow the 0.1% acetic acid in acetonitrile to slowly drip gravimetrically (approximately one drop in 5 seconds).

10.18.3 After the solution has stopped dripping, reapply the vacuum to ensure that the last portion of solvent is collected. <u>This is a very important step</u>.

10.18.4 If two cartridges were used, transfer all extracts into one collection vial and evaporate down to approximately 2.5 mL using a N-Evap. Continue to the next step.

10.19 Bring the extract up to the 5 mL final volume

10.19.1 For method 8330A and 8330B, add the calcium chloride solution to adjust the volume of the collected extract to the mark on the calibrated vial.

10.19.2 For method 8321A, add reagent water to adjust the volume of the collected extract to the mark on the calibrated vial.

10.20 Maintenance

10.20.1 As needed, the inside of the manifold block should be cleaned by washing with soap and water, rinsing with acetonitrile, and wiping with a laboratory tissue.

NOTE: The gasket covers should be checked weekly to ensure there are no signs of contamination showing such as discoloration etc, and to ensure that the gasket cover is not losing its seal.

10.20.2 After each use, the valves and tube caps are removed from the manifold, set to the open position and placed in a jar with acetonitrile and placed in a sonication bath for at least 30 minutes. If samples are suspected to be highly contaminated, a 1:1 mixture of acetonitrile and methylene chloride can be used.

10.20.3 Before and after each use, lines are rinsed with acetonitrile, followed by a water rinse.

10.20.4 Visually inspect lines after use and replace if there is any sign of contamination.

10.21 Troubleshooting

10.21.1 If the vacuum in not strong enough, change the seal on the manifold lid. Also check the pressure relief ball and replace it if cracked.

10.21.2 If a sample clogs the cartridge before a significant volume has been extracted, re-aliquot and re-prep the sample at a dilution. This can be done in the same batch, but the re-prep counts as an additional sample towards the 20 sample batch limit.

10.21.3 Consult a supervisor and/or the QA department with unusual sample matrices.

11.0 <u>Calculations and Data Reduction</u>

11.1 Volume of Surrogate or Spike Extracted = (V_{SA}) x (V_E) ÷ (V_I)

Where:

V_{SA} = Volume of Spike or Surrogate originally added.
V_E = Volume of Sample that was extracted through the cartridge
V_I = Volume of Sample that was originally spiked

Example: 0.1 mL of surrogate standard was added to a 253 mL sample.

During the extraction, the cartridge clogged and only 233 mL of sample was actually extracted.

Vol of Surrogate Extracted = 0.1 mL x 233 mL ÷ 253 mL = 0.092 mL

Therefore the initial volume on the benchsheet should be entered as 233 mL and the volume of surrogate should be entered as 0.092 mL.

11.2 Initial Volume

$$InitialVolume(mL) = \frac{FullBottle(g) - EmptyBottle(g)}{Density(g/mL)}$$

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL policy in DV-QA-005P. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency.

12.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

12.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid- level calibration.

12.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

12.2.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. TNI 2009 requires consecutive passing results. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

12.2.4 Until the IDOC is approved by the QA Manager (or designee); the trainer and trainee must be identified in the batch record.

12.2.5 Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

12.3 Training Requirements

The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. A new analyst must be working under documented supervision prior to approval of the IDOC. Documentation that a new analyst is performing under supervision must be entered into the batch record (View Batch Information) until that analyst's IDOC has been approved by the QA Manager (or designee). See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

13.0 Pollution Control

13.1 Solid phase extraction used for water samples greatly reduces the amount of solvent used compared to liquid/liquid extraction.

13.2 Standards and reagents are prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in the Corporate Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Program."

14.2 The following waste streams are produced when this method is carried out:

14.2.1 Expired Chemicals/Reagents/Standards – Contact Waste Coordinator

14.2.2 Flammable solvent waste – Waste Stream C

14.2.3 Aqueous sample waste - Waste Stream X

14.2.4 Methylene chloride – Waste Stream B

14.2.5 Non-hazardous solid waste such as used cartridges can be disposed of in the regular trash.

NOTE: Radioactive and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

15.0 References / Cross-References

15.1 SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

15.2 Method 3535A, Solid-Phase Extraction (SPE), Revision 1, February 2007.

15.3 Method 8330, Nitroaromatics and Nitramines by High Performance Liquid Chromatography, Revision 0, September 1994.

15.4 Method 8000B, Determinative Chromatographic Separations, Revision 2, December 1996.

15.5 Method 8000C, Determinative Chromatographic Separations, Revision 3, March 2003.

15.6 Method 8330A, Nitroaromatics and Nitramines by High Performance Liquid Chromatography, Revision 1, January 1998.

15.7 Method 8330B, Nitroaromatics, Nitramines, and Nitrate Esters by High Performance Liquid Chromatography, Revision 2, October 2006.

16.0 Method Modifications:

16.1 Modifications from SW-846 8330

16.1.1 Method 8330 prescribes the shelf life for standards as follows:

Standards	Concentration	Shelf Life
Stock standards	1,000,000 µg/L (1,000 ppm)	One year
Intermediate standards	2.5 to 1,000 µg/L	Thirty days
Working standards	1 to 500 µg/L	Daily

This SOP describes the use of 1,000 µg/L and 500 µg/L standards, which are assigned a six-month shelf life based on TestAmerica's experience with these materials.

16.2 Modifications from SW-846 3535A

16.2.1 Method 3535A prescribes a 1 liter sample volume. This SOP describes a 500 mL sample volume.

16.2.2 Method 3535A prescribes a 10 mL acetonitrile wash followed by a 30 mL water wash. This SOP describes a 12 mL methylene chloride wash followed by a 12mL acetonitrile wash, followed by a 24 mL water wash. It is the lab's experience that the methylene chloride wash is helpful in removing interferences from the cartridge packing.

16.2.3 Method 3535A prescribes a 5mL acetonitrile elution. This SOP describes a 2.5 mL elution with approximately 0.1% acetic acid in acetonitrile. The lab has demonstrated increased recoveries for tetryl when this slightly acidic elution

solvent is used. The extract is then brought to a 5 mL final volume with calcium chloride solution.

17.0 Attachments

None

18.0 Revision History

18.1 Revision 8 dated 31 October 2017

- Annual Review

18.2 Revision 7 dated 31 October 2016

- Updated section 3.1 to reflect consistent definition verbiage and reference to the QAM
- Added the paragraph associated to section 6.0 to document supporting equipment IDs
- Revised section 6.2.7 to indicate that non-PFTE tubing is used in lieu of Teflon lines and other verbiage.
- Updated the verbiage in section 6.3 to reflect current Software & Hardware information
- Revised section 7.8.2 removing requirement of sub-aliquoting the standard to match what the standards SOP outlines.
- Updated section 9.1 and subsection to reflect current and consistent verbiage regarding laboratory QA/QC requirements
- Removed reference to AFCEE in section 9.1.2
- Added LCSD required when no MS/MSD to sections 9.5.1 Note and 9.6.2
- Added the note to section 10.6 regarding the need to rotate glassware and extraction positions
- Added the note to section 10.20.1 to reflect the need of gasket cover maintenance
- Added section 10.20.4 to visually inspect lines after use and replace if contaminated
- Updated section 12.1, 12.2 and 12.3 to reflect current and consistent verbiage regarding laboratory method performance requirements.

18.3 Revision 6 dated 12 October 2015

- Section 16 was revised to describe method modifications in more detail.

18.4 Revision 5 dated 14 April 2015

- Annual Technical Review
- Removed reference to DV-LC-0025 “Analysis of Picric Acid by LC/MS/MS” from Section 1. The laboratory no longer maintains this method and SOP. Therefore the procedure was revised to remove the requirement to add 6M HCl to the samples for method 8321A.
- The procedure was revised to change the elution solvent from acetonitrile to 0.1% acetic acid in acetonitrile. This was done to improve the recoveries of tetryl. Section 4.4 was added to document the interference that was observed in tetryl which caused it not to fully elute when acetonitrile was used as the elution solvent. Added Section 16.3 to state this method modification.

- Section 4.5 was added to discuss how samples with sediment can interfere with the procedure.
- Section 10.16.1 was revised to better describe the proper rate of sample loading on the SPE cartridge.
- Added Section 15.5, reference for Method 8000C (required in Arizona)

18.5 Revision 4 dated May 30, 2014

- Annual Technical Review.
- Removed reference to DV-LC-0028 “Analysis of Nitroaromatic and Nitroamine Explosive Compounds by APCI/LC/MS/MS” from Section 1. The laboratory no longer maintains this method and SOP.
- Section 6.1 was revised to remove the requirement to disassemble the valves before soaking them in solvent.
- Section 7.2 was revised to require the testing of acetonitrile on a lot basis.
- Section 7.3 was revised to correct how the 6M HCl is prepared. The reagent is prepared using reagent water, HPLC grade water is not necessary.
- Section 7.9 was revised to instruct the analyst to only remove a portion of the LCS standard from the storage freezer each day.
- Updated table in section 8.0 and removed sections 8.1-8.3 as they were redundant with all info not in table.
- Revised Section 9.1 to state prep SOPs do not include acceptance criteria for QC samples – reference analytical SOPs.
- Section 9.1.2 was revised to state that this procedure meets all criteria of DoD QSM 5.0.
- Removed “Acceptance Criteria” and “Corrective Action” information from Section 9. This information can be found in the analytical SOPs.
- Revised Section 10.3 to include a methylene chloride rinse of the cartridge for method 8330. This was done to remove interferences. Methylene chloride was added to Section 5 Safety, Section 7 Reagents, and Section 14 Waste Management.
- Revised Section 10 to instruct the analyst to filter all samples with visible sediment, removing the instructions to decant samples that have settled solids.
- Added instructions to cap and mix the samples after the addition of the surrogate, spike, and acid or salt.
- Revised the instruction in Section 10.17 on how to prevent cross-contamination from the needles after the sample has been loaded onto the cartridge and before the cartridges have been eluted.
- Added sub-sections for Maintenance and Troubleshooting to Section 10 per DoD QSM 5.0.
- Updated section references to reflect revisions.
- Formatting changes throughout.

18.6 Revision 3 dated May 30, 2013

- Annual Technical Review
- Corrected formatting and grammatical errors.
- Section 6.1 was revised to give more detail on the cleaning of the valves and tube caps. The valves and tube caps should be sonicated in a jar of acetonitrile for at least 30 minutes before use. The jar uses should be replaced at least weekly.
- Section 6.2 was revised to remove aluminum foil and dishes as part of the supply list. These items are not used in the procedure.

- The procedure was revised to define reagent water as water coming from the ELGA purification system. The option for bottled HPLC water was removed. This was done to ensure consistency in the procedure and to reduce the cost and environmental impact of bottled water (shipping, empty bottle waste).
- Sections 10.6, 10.8, 10.9, and 10.10 were revised to instruct analysts to use disposable amber bottles instead of solvent-rinsed beakers. This was done to reduce the chance of cross-contamination and to reduce solvent usage and waste.

18.7 Revision 2.1 dated May 25, 2012

- Annual Technical Review
- Corrected formatting and grammatical errors.
- Updated Section 6.1 to incorporate the addition of 0.1 mL tips used to add surrogate and spike standards to samples.
- Revised Section 7.3 to state that 6M HCl Solution is added prior to extraction, when extracting for method 8321A or 8321B.
- Revised Section 7.7 to state that baked Sodium Chloride is used when extracting for method 8330A or 8330B.
- Updated Section 10.3 to more accurately describe the rinsing of all tubes and ports on the vacuum manifold.
- The instructions for aliquotting samples was moved to be before the instructions on surrogating and spiking the samples to match actual lab practice
- Updated Section 10.16 to include a reference to the Calculation Data Reduction Equation found in Section 11.
- Revised Section 11 to include a detailed equation, with example, on how to calculate the actual surrogate and spike volumes of samples when the extraction cannot be completed after use of a second cartridge.

18.8 Revision 2 dated April 29, 2011

- Revised Section 2.1 to incorporate the addition of NaCl instead of 6M HCL for method 8330A and 8330B.
- Updated Section 6.2 and 10.4 to incorporate a change to the cartridges used for method 8330A and 8330B.
- Added section NaCl to Section 7.
- Revised Section 7.1 to state that reagent water from the ELGA purification system should be 18 to 18.2 Mohm-cm.
- Updated note in section 10.12 to reference WI-DV-0009 for information about surrogate and spike standards.
- Added sections 10.14.1 and 10.14.2 to direct analysts to add hydrochloric acid when extracting for method 8321A or 8321B and to add sodium chloride when extracting for method 8330A or 8330B.
- Removed the Attachments describing the working level surrogate and spike standards. This information is now in DV-OP-0020

Earlier revision histories have been archived and are available upon request.

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